Biomass Conversion and Biorefinery (2020) 10:35–43
https://doi.org/10.1007/s13399-019-00403-7

ORIGINAL ARTICLE

Porous and adsorption properties of activated carbon prepared from cocoa pod husk by chemical activation

Wen-Tien Tsai[1] · Yun-Chi Bai[2] · Yu-Quan Lin[2] · Yi-Ching Lai[2] · Chi-Hung Tsai[3]

Received: 11 December 2018 / Revised: 15 February 2019 / Accepted: 12 March 2019 / Published online: 22 March 2019

Abstract

Utilization of cocoa pod husk (CPH) for the preparation of high-surface-area activated carbon (AC) by using low-pollution potassium hydroxide (KOH) as an activating agent was studied in this work. The thermochemical results of CPH, including the proximate analysis, calorific value, organic and mineral component analyses, showed that the biomass should be a great precursor based on its large percentage of volatile matter and less amount of fixed carbon. A series of activation experiments were conducted to produce activated carbons from dries CPH at different temperatures (i.e., 400, 500, 600, 700, and 800 °C) held for 30 min. To evaluate the potential for adsorbent in removing environmental pollutants, the resulting activated carbons were subject to the analyses of chemical and physical properties, including elemental analysis, true density, surface area/pore volume, and surface morphology by scanning electron microscope (SEM). Based on the pore properties, activation temperature at around 800 °C seemed to be the optimal condition for producing highly microporous AC, where its BET surface area (> 1800 m^2/g) and total pore volume (about 0.95 cm^3/g) largely increased compared with that of the AC produced at 400 °C (ca. 6.0 m^2/g). Based on the adsorption kinetic performance tests, it showed that it is feasible to use the resulting AC as an effectively low-cost adsorbent for the removal of organic compound (e.g., dye) from aqueous solution in comparison with commercial AC.

Keywords Activated carbon · Cocoa pod husk · Chemical activation · Pore property · Adsorption performance

1 Introduction

Cocoa (*Theobroma cacao*) is an economically important crop because it has been used mainly in chocolate manufacturing. During the cocoa bean-producing process, the ripe pods are harvested from the cocoa trees and then broke open for removing wet bean trees. After fermentation of surrounding pulp for draining cocoa pulp juice, the beans are further dried and bagged, constituting the commodity cocoa bean. Cocoa pod husk (CPH), accounting for over 50% of the weight of the cacao fruit [1], is originated from the leftover pod material of the matured cocoa fruit. It was often discarded as waste or residue during the processing of raw cocoa beans on the farm, causing environmental health problems such as greenhouse gas emissions, foul odor, and disease inoculum source due to its lignocellulosic constituents and biological decomposition [2]. Therefore, the cocoa farmers were encouraged to utilize CPH for animal feed and as a source of alkali for soap making aside from its use as a potash (potassium-rich) fertilizer on the cocoa plantation or other crop fields [2–10].

Because about 10 tons of wet CPH are generated from one ton of dry cocoa beans produced, it represents million tons of CPH being disposed of without available utilization every year. More significantly, CPH contains some valuable components such as carbohydrate, protein, fiber, lipid, soluble phenolics, tannin, theobromine (one of the alkaloids), potassium-rich ash, and pectin [2, 11–13]. In recent years, it was further considered as a potential food source of natural components such as dietary fibers with significant antioxidant activity [11], pectins used as gelling/thickening/stabilizing agents [1, 2, 14, 15], and enzyme lipase for biodiesel production [16, 17]. On the other hand, CPH is comprised of lignocellulosic constituents

---

✉ Wen-Tien Tsai
wttsai@mail.npust.edu.tw

[1] Graduate Institute of Bioresources, National Pingtung University of Science and Technology, Neipu Township Pingtung 912, Taiwan

[2] Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 912, Taiwan

[3] Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 640, Taiwan

(i.e., cellulose, hemicellulose, and lignin), showing that it can be served as reinforcement materials or fillers for polymer-based matrices like bioplastics and biocomposites [18–22]. Furthermore, it is rich in carbon source, suggesting that it can be used as an energy source by combustion [23], converted into useful chemicals by pyrolysis [24–26], or directly utilized as an adsorbent for removal of organic compounds and metal ions from aqueous solution [27–32].

Activated carbon (AC) is the most common adsorbent due to its excellent pore properties like high surface area and wide pore size distribution. Regarding its production process by chemical activation method, potassium hydroxide (KOH) is an environment-friendly reagent for the preparation of high-surface-area activated carbon [33]. By contrast, the commonly used chemicals zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4) may generate environmental pollution problems as a result of the releases of chemical activation compounds. As studied by Leite et al. [34], however, it was demonstrated that the contents of Zn leached out with HCl are practically removed from the carbon material. In addition, the KOH activation provides a cleaner process to produce highly microporous carbon material because the solution after the acid washing of crude AC can be reused as a liquid fertilizer.

Since the early 1970s, the uses of cheap agricultural byproducts and environmentally chemical agents have been a focus of research efforts. Due to its high polysaccharides, cocoa-derived residues (i.e., CPH and cocoa bean husk) have recently been utilized as a low-cost precursor for producing AC and its application for the removal of organic compounds from the aqueous solution [35–45]. As reported by Ahmad et al. [35–37], CPH-based AC was produced by carbonization at 800 °C followed by physical activation at 850 °C in a CO_2 flow, showing that the largest surface area of the resulting AC was recorded at about 560 m^2/g. In the similar study by Bello et al. [38], CPH-based AC was produced by carbonization at 500 °C with a heating rate of 10 °C/min followed by CO_2 activation at 700 °C for 2 h, indicating that the surface area of the resulting AC was obtained at 503 m^2/g. In the study by Pereira et al. [39], the resulting ACs were produced by using H_3PO_4 and $ZnCl_2$ at 500 °C with a heating rate of 5 °C/min, showing their surface areas of 1077 and 642 m^2/g, respectively. In the preliminary investigation by Ribas et al. [40], inorganic components, consisting of red mud, lime, KOH, $Al(NO_3)_3$, and Na_2SO_4, were used as chemical-activating agents for producing ACs at 20 °C/min up to 800 °C for 30 min. As studied by Saucier et al. [41], they further used the microwave-induced chemical activation process with similar inorganics for producing ACs, which indicated the BET surface areas ranging from 541 to 619 m^2/g. In the previous study [42], the authors used the acid-leached CPH as a precursor for preparing AC by physical activation at a temperature range of 650–850 °C, showing an increasing BET surface areas from 1 to 638 m^2/g as the temperature increased.

As reviewed above, many studies have reported the utilization of CPH as a precursor for producing AC [35–45]. However, these studies focused on traditional activation processes for producing ACs, which only possess a low-medium surface area (i.e., less than 700 $m^{2/}g$). Previously, the authors thus used potassium salts (i.e., KOH and K_2CO_3) for producing high-surface-area ACs from corn cob [46], convincing that activation temperature is the most important process parameter. Using a small amount of potassium hydroxide (KOH) as chemical activation agent, this study aims to produce a low-cost and high-surface-area AC from the CPH waste, which is rich in potassium salts. Therefore, a series of KOH activation tests were carried out in the production of ACs from CPH. Furthermore, the resulting ACs were performed to observe their variations on the pore properties by means of nitrogen adsorption-desorption isotherms, helium-displacement true densities, elemental analyses, and scanning electron microscopy (SEM). Finally, we evaluated the adsorption kinetic performance for the removal of methylene blue (MB, cationic dye) from aqueous solution using the CPH-based AC in comparison with commercial AC.

2 Materials and methods

2.1 Materials

The CPH used as a precursor for AC preparation was obtained from a local cocoa plantation farm at Neipu Township (Pingtung, Taiwan). Firstly, the collected CPH was crushed to remove attached residues and subsequently sieved to fractions with particle size 0.63 mm on average. Prior to the impregnation pretreatment with KOH, the

Table 1 Proximate analysis and ultimate analysis of cocoa pod husk (CPH)

Property	Value [a]
Proximate analysis (wt%)[a]	
Volatile matter	61.17 ± 0.62
Ash content	8.14 ± 0.03
Moisture content	10.91 ± 0.31
Fixed carbon[b]	19.78
Ultimate analysis (wt%)[c]	
Carbon (C)	41.59 ± 0.03
Hydrogen (H)	6.18 ± 0.06
Oxygen (O)	45.98 ± 0.02
Nitrogen (N)	1.67 ± 0.05
Sulfur (S)	0.10 ± 0.02

[a] Based on the as-received sample; three measurements

[b] By difference

[c] Moisture-free basis; two measurements

Table 2 Ultimate analyses of CPH-based ACs at different activation temperatures (400–800 °C) held for 30 min under the fixed impregnation ratio of 0.5 with KOH

Ultimate analysis (wt%)[a]	CPHAC-400[b]	CPHAC-500	CPHAC-600	CPHAC-700	CPHAC-800
Carbon (C)	78.86[c]	73.38	68.23	64.62	58.57
Nitrogen (N)	2.07	1.79	1.71	0.60	0.41
Hydrogen (H)	3.47	1.62	1.33	1.68	2.87
Sulfur (S)	0.12	0.25	0.34	0.29	0.19
Oxygen (O)[c]	15.48	22.96	31.81	32.81	37.96

[a] Dry basis

[b] CPH-based AC produced at 400 °C, etc.

[c] By difference

dried CPH has been preserved in a desiccator. The proximate properties (i.e., volatile, ashes, and fixed carbon) of the dried CPH have been determined by using the American Society for Testing and Materials (ASTM) Standard Test Methods (i.e., D-3172). Table 1 listed the thermochemical properties of the feedstock, showing that the as-received CPH consists largely of volatile matter (i.e., 61.17 wt%), but the content of ash in the sample reaches as high as 8.14 wt%. These results are similar to those by the previous study [42] and other studies [11, 47]. The cationic dye used as the target adsorbate in the present study is methylene blue (MB), which was purchased from Merck Co. (Germany). A commercial AC (FILTRASORB 300, named as Calgon-300 in this work) from Calgon Carbon Co. (USA) was used as an adsorbent for removal of MB at the same adsorption conditions. Its main pore properties are given below: BET surface area 660 m^2/g, total pore volume 0.38 cm^3/g, and average pore diameter (by the analytical data on BET surface area and total pore volume) 2.32 nm.

2.2 Chemical activation experiments

In the previous study [48], the temperature of 500 °C was found to be optimal for preparing high-surface-area AC from corn cob by $ZnCl_2$ activation. Prior to KOH activation experiments at 500 °C in this work, 10 g of the dried CPH was well mixed with 150 mL deionized water and 2.5–10.0 g KOH (Merck Co.; Assay ≥ 85.0%) in 250 mL Erlenmeyer flasks using sealing film. Impregnation was carried out on a thermostat agitator at about 30 °C for 1 h. Afterward, the impregnated sample solution was placed into a heated air circulation oven to leave KOH-impregnated CPH by removal of water. Then, the influences of the impregnation ratios (i.e., 0.25, 0.50, 0.75, and 1.00 g KOH/g CPH) at a fixed holding time (i.e., 30 min)

Table 3 Pore properties and densities of CPH-based ACs at different activation temperatures (400–800 °C) held for 30 min under the fixed impregnation ratio of 0.5 with KOH

Property	CPHAC-400	CPHAC-500	CPHAC-600	CPHAC-700	CPHAC-800
BET surface area (m^2/g)[a]	6.0	483.0	744.0	1162.0	1783.0
Micropore surface area (m^2/g)[b]	2.4	396.5	658.6	1031.6	1224.0
Total pore volume (cm^3/g)[c]	0.0083	0.2664	0.3692	0.6193	0.9488
Micropore volume (cm^3/g)[d]	0.0012	0.2022	0.3357	0.5270	0.6230
Pore diameter (Å)[e]	55.6	22.1	21.3	21.3	21.3
Porosity (−)[f]	0.0118	0.3071	0.4137	0.6342	0.7760
True density (g/cm^3)[g]	1.4297	1. 6638	1.9109	2.7995	3.4947
Particle density (g/cm^3)[h]	1.4129	1.1528	1.1204	1.0241	0.8179

[a] BET surface area based on the relative pressure (P/P_0) ranging from 0.05 to 0.30

[a] Micropore area by *t*-plot method

[c] Total pore volume obtained at relative pressure of about 0.95

[d] Micropore volume by *t*-plot method

[e] Estimated by the values of BET surface area and total pore volume

[f] Estimated by the values of particle density and true density [49, 50]

[g] Measured by a pycnometer

[h] Estimated by the values of total pore volume and true density [49, 50]

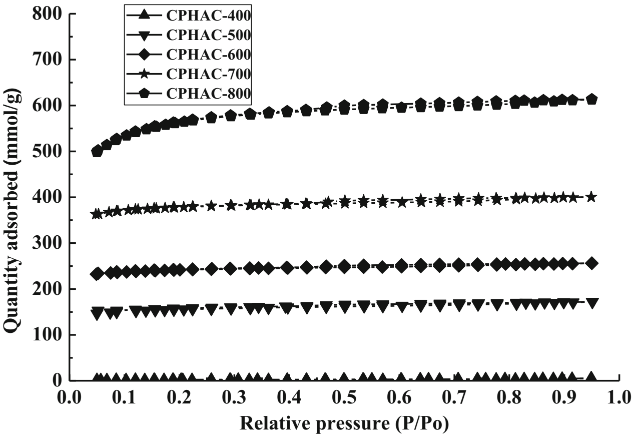


Fig. 1 N_2 adsorption-desorption isotherms of cocoa pod husk–derived activated carbon (CPHAC) products (i.e., CPHAC-400, CPHAC-500, CPHAC-600, CPHAC-700, and CPHAC-800)

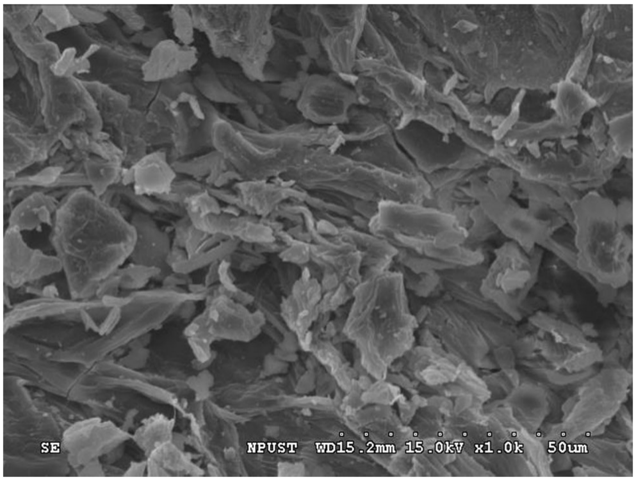


Fig. 3 SEM image of cocoa pod husk (CPH, × 1000)

and holding times (i.e., 15, 30, 45, and 60 min) at a fixed impregnation ratio (i.e., 0.50 g KOH/g CPH) on the pore properties of the resulting ACs were preliminarily studied. The data on the BET surface areas of the resulting ACs, ranging from 458.4 to 534.4 m^2/g, varied without being consistent with the impregnation ratio and holding time. Those instances will suggest that these activation parameters are not significant factors that affect the pore properties of the AC products.

In the subsequent KOH activation experiments, the activation temperature was only adopted in the production of AC because it has the greatest influence on chemical activation. The AC products were prepared from the pyrolysis of the KOH-impregnated CPH sample (4 g, in each set of experiments) as reported previously [48]. For all tests, the CPH sample was heated to 400–900°C in the presence of nitrogen gas (500 cm^3/min) at about 10 °C/min, after which the temperature was held for 30 min before cooling to room temperature. The crude solid products after KOH activation were then rinsed with 3 N HCl and deionized water 3–5 times to remove potassium ions and other residues remained. Finally, the resulting products were dried overnight in an oven at about 100 °C. The resulting ACs prepared at 400, 500, 600, 700, and 800 °C were thus referred to as CPHAC-400, CPHAC-500, CPHAC-600, CPHAC-700, and CPHAC-800, respectively. In order to obtain AC with a higher yield, another resulting AC (CPHAC) was prepared at 800 °C for 0.5 h under the impregnation ratio of 0.75 g KOH/g CPH. This AC product was used to test its adsorption performance for removal of cationic dye (i.e., MB) from aqueous solution in comparison with commercial AC.

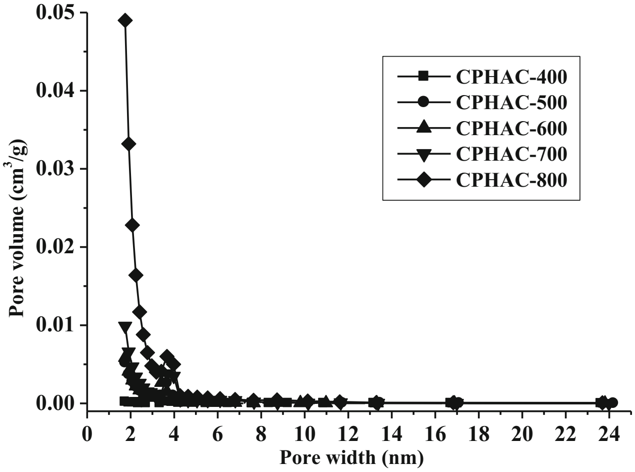


Fig. 2 Pore size distributions of cocoa pod husk–derived activated carbon (CPHAC) products (i.e., CPHAC-400, CPHAC-500, CPHAC-600, CPHAC-700, and CPHAC-800)

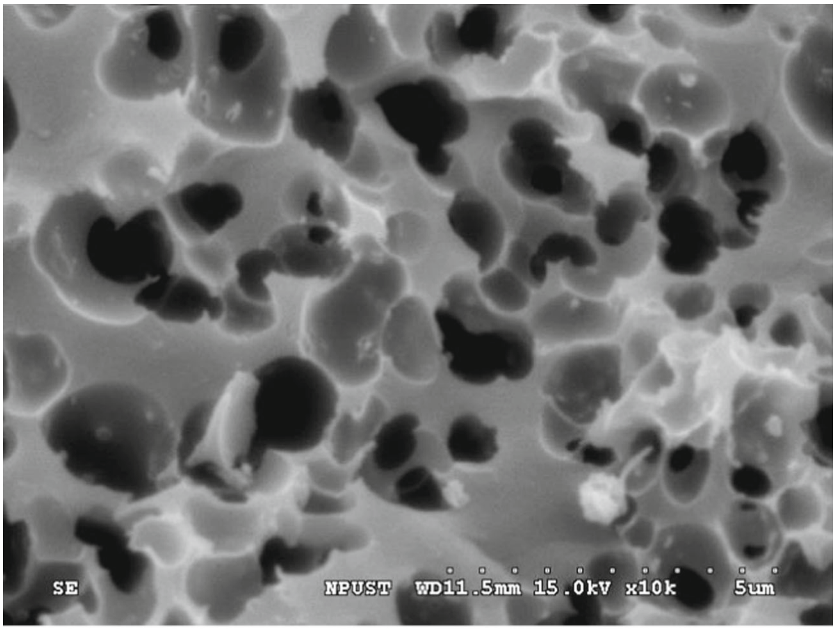
2.3 Characterization of CPH-based activated carbons

Based on the measurement using a surface area and porosity analyzer (model no.: ASAP 2020; Micromeritics Co., USA), the pore properties of CPH-based ACs can be determined. The specific surface area of the resulting AC was based on the Brunauer-Emmett-Teller (BET) standard method, giving a straight line in the relative pressure (P/P_0) range of 0.05–0.30. The total pore volume was obtained from the liquid nitrogen amount adsorbed at P/P_0 of about 0.95 [49]. Furthermore, the mean pore size can be estimated by using the measured BET and pore volume [50]. Using the Barrett-Joyner-Halenda (BJH) method at desorption branch, their pore size distributions were further determined in the range of 2.0–25.0 nm.

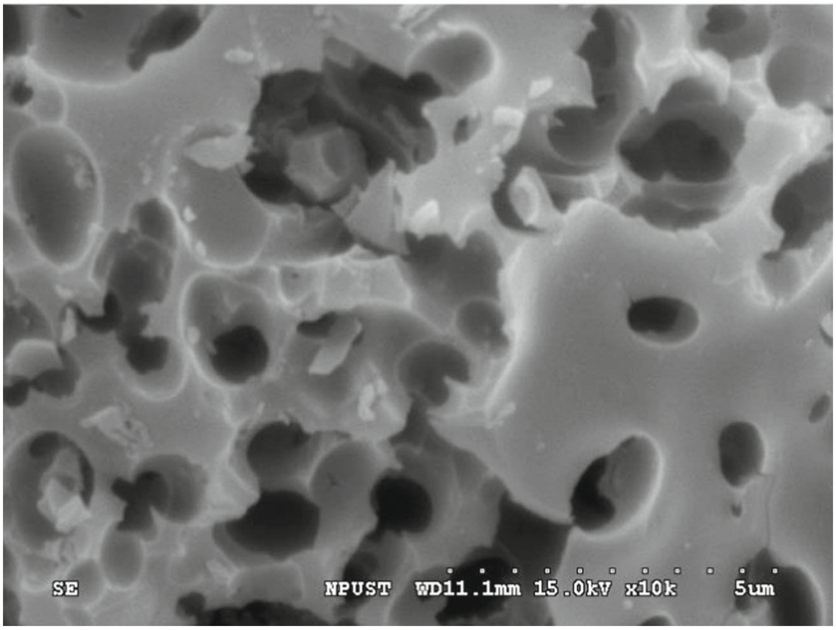
The true density (also called absolute density or helium-displacement density) of the resulting AC product was obtained by a gas pycnometer (model no.: AccuPyc 1340; Micromeritics Co., USA), which is based on the principle of helium displacement. The instrument features high-resolution pressure transducers and a thermoelectric

Fig. 4 SEM images of CPHAC product (**a**) (i.e., CPHAC-700, × 10,000) and optimal CPHAC product (**b**) (i.e., CPHAC-800, × 10,000)

(a) CPHAC-700 (×10,000)



(b) CPHAC-800 (×10,000)



device to deliver temperature stability. The data on true density will be further used to calculate its particle density and porosity [50].

Due to the pore properties of CPH-based ACs associated with their contents of carbon and other organic elements, the elemental analyses of these resulting ACs (about 3 mg for each analysis) were conducted using an elemental analyzer (model: vario EL III; Elementar Co., Germany). In terms of its main elements of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S), the oxygen content was estimated by the difference (i.e., O = 100%−C−H−N−S).

The surface textures of CPH and CPH-based ACs were carried out using a scanning electron microscopy (model no.: S-3000N; Hitachi Co., Japan). These observations were operated at an accelerating potential of 15 kV. Prior to the image work, a thin film of gold (Au) was coated on the sample

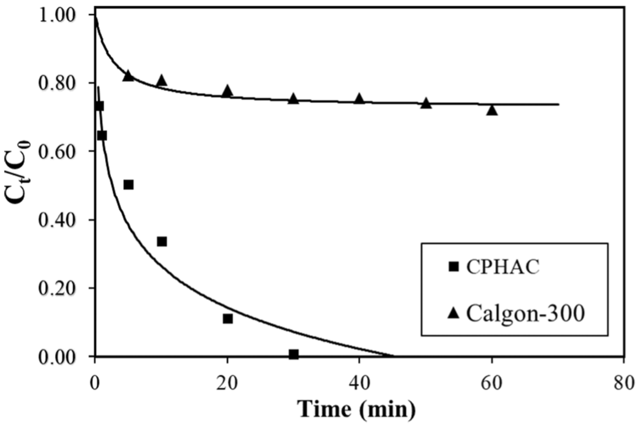


Fig. 5 Plots of dimensionless concentration (C_t/C_0) vs. time for the resulting AC (CPHAC) and commercial AC (Calgon-300); Adsorption conditions: initial MB concentration = 10 mg/L (or 3.13×10^{-2} mol/L), adsorbent dosage = 0.2 g/2 L, adsorption temperature = 25 °C, and agitation speed = 200 rpm; symbols: experimental data, full lines: calculated from Eq. (1) and Table 4

to form an electrically conductive surface using an ion sputter (model no.: E1010; Hitachi Co., Japan).

2.4 Adsorption performance test of CPH-based activated carbon

In the present study, the adsorption performance of the CPH-based AC (i.e., CPHAC) was carried out in a 3-L stirred batch adsorption apparatus with four baffles in comparison with the commercial AC (Calgon-300). The adsorption kinetic behaviors of methylene blue (MB) from aqueous solution were obtained under the initial MB concentration of 10 mg/L (or 3.13×10^{-2} mol/L), adsorbent dosage of 0.2 g/2 L, agitation speed of 200 rpm, and temperature of 25 °C. The solution sample (about 10 cm^3) was taken at a specified time up to 1 h and then filtrated with fiber membrane (cat. no.: A045A025A; ADVANTEC MFS, Inc., Japan). The MB concentration analysis of the filtrate solution was immediately measured with UV/Visible spectrophotometer (model: U-2001; Hitachi Co., Japan) at 661-nm wavelengths. The amount of MB adsorbed (q_t, mg/g) was thus determined by the solution volume (i.e., 2 L), adsorbent mass, and the difference of initial MB concentration (C_0) and MB concentration at adsorption time (C_t).

3 Results and discussion

3.1 Elemental analyses of CPH-based activated carbons

Table 2 provided the data on the elemental analysis of the resulting ACs produced from CPH. It is obvious that the CPH-based AC products contained high contents of carbon (C) and oxygen (O), which should be attributed to the lignocellulosic composition and ash content of CPH. In comparison, the elemental content of a typical AC was found to be 88 wt% C [51]. As described in Table 1, the content of C in the CPH precursor was around 41.6 wt%, which was smaller than those of CPH-based ACs (i.e., 58.57–78.86 wt%). It should be noted that the contents of oxygen (O) in the resulting ACs indicated an increasing trend, which should be attributed to the fact that more potassium carbonates and oxides were likely remained at higher activation temperature. Furthermore, more oxygen-containing functional groups could be present on the surface of the resulting AC, thus indicating a negatively charged surface. On the other hand, there is no correlation between hydrogen content (i.e., 1.05–2.18 wt%) and activation temperature.

3.2 True densities of CPH-based activated carbons

The true density (ρ_s) is related to its hardness or compressive strength because the increased order of carbon molecules indicated higher resistance strength than its starting material. The increase in rigid and porous structures was caused by the significant loss of volatiles and condensable compounds from the original feedstock. Consequently, the data on true density of CPH-based AC indicated an increasing trend with activation temperature, ranging from 1.430 g/cm^3 for CPHAC-400 to 3.495 g/cm^3 for CPHAC-800 as shown in Table 3. In this respect, the true density of CPH-based AC can be used as an appropriate indicator for its extents of condensation and shrinkage during the activation process. Furthermore, it seemed that there exists a close connection between the true density and pore property.

Table 4 Kinetic parameters for adsorption of methylene blue (MB) onto the resulting AC (CPHAC) and commercial AC (Calgon-300) based on pseudo-second-order model[a]

Adsorbent	Adsorption kinetic parameter[b]			Pore property of adsorbent	
	q_e (mg/g)	k (g/(mg min))	R^2	BET surface area (m^2/g)	Total pore volume (cm^3/g)
CPHAC	109.9	2.333×10^{-3}	0.994	1257	0.69
Calgon-300	27.40	1.334×10^{-2}	0.991	660.1	0.38

[a] Adsorption conditions: initial MB concentration = 10 mg/L (or 3.13×10^{-2} mol/L), adsorbent dosage = 0.2 g/2 L, agitation speed = 200 rpm, and temperature = 25 °C

[b] Based on the pseudo-second-order model

3.3 Pore properties of CPH-based activated carbons

Table 3 also indicated the variations of pore properties of CPH-based AC with activation temperature. Obviously, the BET surface area of CPH-based AC significantly increased to 483.0 m^2/g (CPHAC-500) after KOH activation was performed at a temperature range from 400 to 500 °C. The pore properties of the resulting ACs continuously increased in line with the activation temperature. The findings were in accordance with those of studying KOH activation for olive stone [52], cherry stone [53], and grape seed [54]. Porosity in carbons activated at 400 °C is very low, whereas temperatures of 700 and 800 °C lead to activated carbons with increasing porosity, thus suggesting a critical temperature range of KOH activation for producing high-surface-area ACs greater than 1000 m^2/g. Also, a reproducibility test in the chemical activation experiments was examined at the carbon products of CPHAC-400 and CPHAC-700 in duplicate and in triplicate, respectively. The finding showed that their BET surface areas were very consistent based on the values of 6.9 ± 1.3 m^2/g and 1154.6 ± 7.9 m^2/g, respectively.

The nitrogen (N_2) adsorption-desorption isotherm is a powerful tool for the characterization of porous materials like AC. Figures 1 and 2 showed the N_2 adsorption-desorption isotherms (at − 196 °C) and pore size distribution curves of CPH-based AC products, respectively. Obviously, the resulting ACs possessed type I isotherms because they are often encountered in the case of physical adsorption on microporous materials with the pore width less than 2 nm [49]. The micropore filling was observed at relatively low relative pressures (less than 0.05) because of the high adsorption potential [49]. Therefore, the adsorbed values significantly increased at above 700 °C, which should be attributable to the rigorous reaction, creating more fine pores in the resulting carbon products (i.e., CPHAC-700 and CPHAC-800). However, beyond 800 °C, there could be less increase in the development of pores due to pore collapse, not favorable for their pore properties [55]. To assure the assumption in the KOH activation experiments, the CPHAC-850 and CPHAC-900 (not listed in Table 3) were produced at 850 and 900 °C, respectively. It showed that the BET surface area of the former increased slightly to about 1850 m^2/g, but the latter decreased significantly due to serious burn-off. Li et al. [56] also found similar results in the preparation of ACs from poplar wood by KOH activation at a higher temperature (> 750 °C).

3.4 SEM observations of CPH-based activated carbons

Figure 3 showed the SEM micrograph of CPH (× 1000) for the observation of the surface texture of the biomass sample. As observed in the sample of dried CPH, it exhibited a heterogeneous surface as it is expected of fibrous agricultural residue. In contrast, the CPHAC-700 and CPHAC-800 products in Fig. 4 displayed porous or pitted surface textures at the scale of a macropore with > 50 nm, indicating that rigorous activation reaction with KOH took place at these carbon materials. In brief, the production conditions at the higher activation temperature will develop more fine pores in the carbon products, thus resulting in the increasing trends of pore properties and true densities as listed in Table 3.

3.5 Adsorption performance of CPH-based activated carbon

Figure 5 showed the adsorption kinetic profiles of two adsorbents (i.e., CPHAC and Calgon-300) for removal of MB from aqueous solution at initial MB concentration of 10 mg/L (or 3.13×10^{-2} mol/L), adsorbent dosage of 0.2 g/2 L, agitation speed of 200 rpm, and temperature of 25 °C. Obviously, the fast decrease in residual MB concentration (C_t/C_0) can be seen at a short contact time, especially in the adsorbent CPHAC. It implied that the strong interaction should exist between the cationic dye and the negatively charged surface. Therefore, a simple model (i.e., pseudo-second-order equation) was used to fit the adsorption kinetic data in this work [57]. Its linear form was given below:

$$t/q_t = 1/\left(k \times {q_e}^2\right) + (1/q_e) \times t \tag{1}$$

where q_t is the amount of MB removed at time t (mg/g), q_e is the amount of MB adsorbed at equilibrium (mg/g), k is the pseudo-second-order rate constant (g/(mg min)), and t is the contact time (min). The fitted values of parameters for the adsorption system have been listed in Table 4, indicating that the correlation between the experimental and fitting results was great. As observed in Fig. 5, the adsorbent CPHAC exhibited a better adsorption performance for MB removal as compared with the commercial AC (Calgon-300) in spite of their similar pore properties. This difference in adsorption capacity can be also attributable to the interaction between the cationic adsorbate and the adsorbent on the surface nature [58]. Obviously, the adsorbent CPHAC has a stronger interaction in comparison with the adsorbent Calgon-300.

4 Conclusions

A series of AC products were prepared from dried cocoa pod husk (CPH) using KOH activation process. According to the chemical, pore, and adsorption properties of the CPH-based ACs, the following conclusions below can be drawn:

- The pore development of the resulting AC was mainly determined by the process temperature. The true densities of the CPH-based ACs indicated an increasing trend with activation temperature, thus suggesting a more rigid and porous carbon material produced at higher activation temperatures.
- The optimal AC product produced at around 800 °C showed its BET surface area of over 1800 m^2/g and the total pore volume of about 1.0 cm^3/g.
- It has been shown that the microporous features (i.e., pore width is less than 2.0 nm) of the resulting ACs were based on their nitrogen adsorption-desorption isotherms.
- The CPH-based AC can be an effective low-cost adsorbent from aqueous solution in comparison with commercial AC based on the fitting results of pseudo-second-order model for adsorption removal of cationic dye (i.e., methylene blue).

Acknowledgements The authors express sincere appreciation to the Instrument Centers of National Chung Hsing University and National Pingtung University of Science and Technology for their assistance in elemental analysis and scanning electron microscope (SEM) observation, respectively.

Funding information The authors thank the Pingtung County Government (Taiwan) and Wel-Han Environmental Industrial Co. (Pingtung County Government, Taiwan) for providing financial support for this work.

References

1. Vriesmann LC, Teofilo RF, Petkowicz CLO (2012) Extraction and characterization of pectin from cacao pod husks (*Theobroma cacao* L.) with citric acid. LWT–Food Sci Technol 49:108–116
2. Vriesmann LC, Amboni RDMC, Petkowicz CLO (2011) Cacao pod husks (*Theobroma cacao* L.): composition and hot-water-soluble pectins. Ind Crop Prod 34:1173–1181
3. Donkoh A, Atuahene CC, Wilson BN, Adomako D (1991) Chemical composition of cocoa pod husk and its effect on growth and food efficiency in broiler chicks. Anim Feed Sci Technol 35: 161–169
4. Osei SA, Atuahene CC, Heathcote D, Frimpong EB, Adomako D (1991) Cocoa pod and husk meal as a feed ingredient in layer diets. Anim Feed Sci Technol 35:283–288
5. Alawa JP, Umunna NN (1993) Alternative feed formulation in the developing countries: prospects for utilization of agro-industrial by-products. J Anim Prod Res 13:63–98
6. Ridzwan BH, Fadzli MK, Rozali MBO, Chin DTF, Ibrahim BM, Faridnordin BI (1993) Evaluation of cocoa-pod husks on performance of rabbits. Anim Feed Sci Technol 40:267–272
7. Taiwo OE, Osinowo FAO (2001) Evaluation of various agro-wastes for traditional black soap production. Bioresour Technol 79:95–97
8. Moyin-Jesu EI (2007) Use of plant residues for improving soil fertility, pod nutrients, root growth and pod weight of okra (*Abelmoschus esculentum* L). Bioresour Technol 98:2057–2064
9. Oddoye EOK, Rhule SWA, Agyente-Badu K, Anchirinah V, Owusu Ansah F (2010) Fresh cocoa pod husk as an ingredient in the diets of growing pigs. Sci Res Essay 5:1141–1144
10. Ashade OO, Osineye OM (2013) Effect of replacing maize with cocoa pod husk in the nutrition of *Oreochromis niloticus*. J Fish Aquat Sci 8:73–79
11. Martinez R, Torres P, Meneses MA, Figueroa JG, Perez-Alvarez JA, Viuda-Martos M (2012) Chemical, technological and in vitro antioxidant properties of cocoa (*Theobroma cacao*) co-products. Food Res Int 49:39–45
12. Oddoye EOK, Agyente-Badu CK, Gyedu-Akoto E (2013) Cocoa and its by-products: identification and utilization. In: Watson RR, Preedy VR, Zibadi S (eds) Chocolate in health and nutrition. Springer, New York, pp 23–37
13. Betiku E, Etim AO, Pereao O, Ojumu TV (2017) Two-step conversion neem (Azadirachta indica) seed oil into fatty methyl esters using a heterogeneous biomass-based catalyst: an example of cocoa pod husk. Energy Fuel 31:6182–6193
14. Chan SY, Choo WS (2013) Effect of extraction conditions on the yield and chemical properties of pectin from cocoa husks. Food Chem 41:3752–3758
15. Priyangini F, Walde SG, Ramalingam C (2018) Extraction optimization of pectin from cocoa pod husks (*Theobroma cacao L.*) with ascorbic acid using response surface methodology. Carbohydr Polym 202:497–503
16. Khanahmadi S, Yusof F, Ong HC, Amid A, Shah H (2016) Cocoa pod husk: a new source of CLEA-lipase for preparation of low-cost biodiesel: an optimized process. J Biotechnol 231:95–105
17. Odude VO, Adesina AJ, Oyetunde OO, Adeyemi OO, Ishola NB, Etim AO, Betiku E (2017) Application of agricultural waste-based catalysts to transesterification of esterified palm kernel oil into biodiesel: a case of banana fruit peel versus cocoa pod husk. Waste Biomass Valoriz. https://doi.org/10.1007/s12649-017-0152-2
18. Okieimen FE, Imanah JE (2006) Studies in the utilization of agricultural waste products as filler in natural rubber compounds. J Appl Polym Sci 100:2561–2564
19. Bayer IS, Guzman-Puyol S, Heredia-Guerrero JA, Ceseracciu L, Pignatelli F, Ruffilli R, Cingolani R, Athanassiou A (2014) Direct transformation of edible vegetable waste into bioplastics. Macromolecules 47:5135–5143
20. El-Shekeil YA, Sapuan SM, Algrafi MW (2014) Effect of fiber loading on mechanical and morphological properties of cocoa pod husk fibers reinforced thermoplastic polyurethane composites. Mater Des 64:330–333
21. Chun KS, Husseinsyah S, Osman H (2015) Utilization of cocoa pod husk as filler in polypropylene biocomposites: effect of maleated polypropylene. J Thermoplast Compos Mater 28:1507–1521
22. Koay SC, Chan MY, Pang MM, Tshai KY (2018) Influence of filler loading and palm oil-based green coupling agent on torque rheological properties of polypropylene/cocoa pod husk composites. Adv Polym Technol 37:2246–2252
23. Syamsiro M, Saptoadi H, Tambunan BH, Pambudi NA (2012) A preliminary study on use of cocoa pod husk as a renewable source of energy in Indonesia. Energy Sustain Dev 16:74–77
24. Mansur D, Tago T, Masuda T, Abimanyu H (2014) Conversion of cocoa pod husks by pyrolysis and catalytic reaction to produce useful chemicals. Biomass Bioenergy 66:275–285
25. Tsai CH, Tsai WT, Liu SC, Lin YQ (2018) Thermochemical characterization of biochar from cocoa pod husk prepared at low pyrolysis temperature. Biomass Conv Bioref 8:237–243
26. Adjin-Tetteh M, Asiedu N, Dodoo-Arhin D, Karam A, Amaniampong PN (2018) Thermochemical conversion and characterization of cocoa pod husks a potential agricultural waste from Ghana. Ind Crop Prod 119:304–312
27. Fiset JJ, Tyagi RD, Blais JF (2002) Cocoa shells as adsorbent for metal recovery from acid effluent. Water Qual Res J Can 37:379–388

28. Bello OS, Ahmad MA (2011) Adsorptive removal of a synthetic textile dye using cocoa pod husk. Toxicol Environ Chem 93:1298–1308
29. Njoku VO, Ayuk AA, Oguzie EE, Ejike EN (2012) Biosorption of cd (II) from aqueous solution by cocoa pod husk biomass: equilibrium, kinetic, and thermodynamic studies. Sep Sci Technol 47:753–761
30. Theivarasu C, Mylsamy S (2012) Adsorption studies of acid blue-92 from aqueous solution by activated carbon obtained from agricultural industrial waste-cocoa (*Theobroma cacao*) shell. Asian J Chem 24:2187–2190
31. Pua FL, Sajab MS, Chia CH, Zakaria S, Rahman IA, Salit MS (2013) Alkaline-treated cocoa pod husks as adsorbent for removing methylene blue from aqueous solutions. J Environ Chem Eng 1: 460–465
32. Njoku VO (2014) Biosorption potential of cocoa pod husk for the removal of Zn (II) from aqueous phase. J Environ Chem Eng 2: 881–887
33. Marsh H, Rodriguez-Reinoso F (2006) Activated carbon. Elsevier, Amsterdam
34. Leite AJB, Sophia AC, Thue PS, dos Reis GS, Dias SLP, Lima EC, Vaghetti JCP, Pavan FA, de Alencar WS (2017) Activated carbon from avocado seeds for the removal of phenolic compounds from aqueous solutions. Desalin Water Treat 71:168–181
35. Ahmad F, Daud WMAW, Ahmad MA, Radzi R (2011) Using cocoa (*Theobroma cacao*) shell-based activated carbon to remove 4-nitrophenol from aqueous solution: kinetics and equilibrium studies. Chem Eng J 178:461–467
36. Ahmad F, Daud WMAW, Ahmad MA, Radzi R (2012) Cocoa (*Theobroma cacao*) shell-based activated carbons by CO_2 activation in removing of cationic dye from aqueous solution: kinetics and equilibrium studies. Chem Eng Res Des 90:1480–1490
37. Ahmad F, Daud WMAW, Ahmad MA, Radzi R, Azmi AA (2013) The effect of CO_2 activation, on porosity and surface functional groups of cocoa (*Theobroma cacao*) – shell based activated carbon. J Environ Chem Eng 1:378–388
38. Bello OS, Siang TT, Ahmad MA (2012) Adsorption of remazol brilliant violet-5R reactive dye from aqueous solution by cocoa pod husk-based activated carbon: kinetics, equilibrium and thermodynamic studies. Asia Pac J Chem Eng 7:378–388
39. Pereira RG, Veloso CM, da Silva NM, de Sousa LF, Bonomo RCF, de Souza AO, Souza MOG, Fontan RCI (2014) Preparation of activated carbons from cocoa shells and siriguela seeds using H_3PO_4 and $ZnCl_2$ as activating agents for BSA and α-lactalbumin adsorption. Fuel Process Technol 126:476–486
40. Ribas MC, Adebayo MA, Prola LDT, Lima EC, Cataluna R, Feris LA, Puchana-Rosero MJ, Machado FM, Pavan FA, Calvete T (2014) Comparison of a homemade cocoa shell activated carbon with commercial activated carbon for the removal of reactive violet 5 dye from aqueous solutions. Chem Eng J 248:315–326
41. Saucier G, Adebayo MA, Lima EC, Cataluna R, Thue PS, Prola LDT, Puchana-Rosero MJ, Machado FM, Pavan FA, Dotto GL (2015) Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. J Hazard Mater 289:18–27
42. Tsai WT, Huang PC (2018) Characterization of acid-leaching cocoa pod husk (CPH) and its resulting activated carbon. Biomass Conv Bioref 8:521–528
43. Plaza-Recobert M, Trautwein G, Perez-Cadenas M, Alcaniz-Monge J (2017) Preparation of binderless activated carbon monoliths from cocoa bean husk. Microporous Mesoporous Mater 243: 28–38
44. Perez-Cadenas M, Plaza-Recobert M, Trautwein G, Alcaniz-Monge J (2018) Development of tailored mesoporosity in carbonized cocoa bean husk. Microporous Mesoporous Mater 256:128–139
45. Rodriguez MH, Yperman J, Carleer R, Maggen J, Vanderheyden S, Hernandez JF, Calvis AO, Gryglewicz G (2018) Evaluation of activation parameters of activated carbon from coffee and cocoa seed husk rests: carbon yields and Ni(II) adsorption capacity study. Desalin Water Treat 104:175–188
46. Tsai WT, Chang CY, Wang SY, Chang CF, Chien SF, Sun HF (2001) Preparation of activated carbons from corn cob catalyzed by potassium salts and subsequent gasification with CO_2. Bioresour Technol 78:203–208
47. Titiloye JO, Baker MSA, Odetoye TE (2013) Thermochemical characterisation of agricultural wastes from West Africa. Ind Crop Prod 47:199–203
48. Tsai WT, Chang CY, Lee SL (1998) A low cost adsorbent from agricultural waste corn cob by zinc chloride activation. Bioresour Technol 64:211–217
49. Lowell S, Shields JE, Thomas MA, Thommes M (2006) Characterization of porous solids and powders: surface area, pore size and density. Springer, Dordrecht
50. Smith JM (1981) Chemical engineering kinetics, 3rd edn. McGraw-Hill, New York
51. Bansal RC, Donnet JB, Stoeckli F (1988) Active carbon. Marcel Dekker, New York
52. Molina-Sabio M, Rodriguez-Reinoso F (2004) Role of chemical activation in the development of carbon porosity. Colloid Surf A 241:15–25
53. Olivares-Marin M, Fernandez-Gonzalez C, Macias-Garcia A, Gomez-Serrano V (2006) Preparation of activated carbons from cherry stones by activation with potassium hydroxide. Appl Surf Sci 252:5980–5983
54. Okman I, Karagoz S, Tay T, Erdem M (2014) Activated carbons from grape seeds by chemical activation with potassium carbonate and potassium hydroxide. Appl Surf Sci 293:138–142
55. Adinata D, Daud WMAW, Aroua MK (2007) Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3. Bioresour Technol 98:145–149
56. Li Z, Gao X, Wu L, Wang K, Kobayashi N (2017) Preparation of activated carbons from poplar wood by chemical activation with KOH. J Porous Mater 24:193–202
57. Ho YS, Chiang CC, Hsu YC (2001) Sorption kinetics for dye removal from aqueous solution using activated clay. Sep Sci Technol 36:2473–2488
58. Brady M, McKay G (1995) Characterization of adsorbents. In: McKay G (ed) Use of adsorbents for the removal of pollutants from wastewaters. CRC Press, Boca Raton, pp 39–58